Organics and Metal Solubility in California Forest Soils

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The role of soluble organics in the dissolution of metals, especially Al, in forest soils of California is the focus of this report. The effects of changing acidity on organo-metal complexation also are reported and discussed with reference to impacts of acidic atmospheric deposition. Soluble organics from forest litter were separated and quantified into acid, neutral and base compounds by exchange-resin techniques, and specific free organic acids were determined by HPLC techniques. The Al in leachates was fractionated using a resin exchange procedure at different pH. Effective metal-complexing organic acids were found to be those that form 5- to 6-membered ring-structures. Using a mobile-phase ion-pairing chromatographic technique, we found that Al has greatest affinity with phenolic functional groups in acid regimes (pH 4.5), but in less acid regimes (pH 5.7) Al has greatest affinity with carboxylic functional groups. Most of the solubilized Al comes from the organically-bound Al fraction of the soil and less from the litter. The simple organic acids in soil solutions sampled in the field rapidly disappear, presumably due to abiotic oxidative polymerization as well as by reaction with organic reductants. These rapid processes necessitate special techniques of preserving field soil solution sampled by lysimetry.

INTRODUCTION

Litter and soil organic matter are extremely important to the water and nutrient regimes and the structure of forest soils. Thus, an understanding of their role and functioning is a prerequisite to the implementation of sustainable forest management practices and to documentation of other environmental perturbations that change their nature or amount. Soluble organics leached from litter and soil organic matter are often the main agents of soil metal-solubility, thus highlighting their importance in pedology, and to an understanding of the bioavailability and toxicity of potentially hazardous metals such as aluminum (Al) (Bache 1986).

Soil organic matter has been studied for many years, but interactions between soil minerals, natural organic compounds and microbes have typically been studied in separate, isolated disciplines in the past. Recent interest in environmental degradation and in alternative management of agricultural and forest resources calls for an integrated approach. This, coupled with the availability of advanced analytical and computer technology, has resulted in a new focus on the chemical, biological and physical behavior of litter and soil organic matter in relation to other soil characteristics and to associated ecosystem components (Bloom 1981, Huang and Schnitzer 1986, McColl 1984).

In a recent review, McKeague *et al.* (1986) listed major gaps in current knowledge related to organo-mineral complexing in soils. Our report is primarily a summary of the integrated work from our laboratory, and our aim has been to fill some of these gaps as they relate to forest soils. Thus our general objectives have been:

1. To gain information on the nature, concentration, and persistence of organic ligands formed during the breakdown of forest litter. We have placed emphasis on the low-molecular-weight aliphatic and phenolic acids. As McKeague *et al.* (1986) pointed out, the "near-fossil" products of decomposition such as fulvic and humic acids have been overemphasised in the past.
2. To study interactions of major organic ligands with mineral soil components, check results from simple laboratory experiments against those obtained in the more-complicated system of soil, and determine the nature and mobility of organo-metal complexes (especially Al) in forest soil.
3. To document the composition of soil solutions from the field, and examine effects of different environmental conditions and management practices. This is a continuing phase of our work.

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Results of both field and laboratory experiments are described, with special reference to the influence of pH. Soluble organic acids are characterized by their metal-chelating abilities, and mechanisms of metal solubilization are explored. The rapid disappearance of simple soluble organic acids from field soil solutions is documented, and the mechanisms involved in their rapid transformations also are explored.

ORGANICS, ACIDITY AND CATION LEACHING

Dissolved Organics In Forested Ecosystems

Dissolved organic carbon (DOC) is transported with rain, passing through a forest canopy and downward through the litter and soil profile (Table 1). Determinations of DOC were made on acidified (pH 2) samples using a Dohrman carbon-analyzer with an infra-red detector. Highest concentrations occur in stem flow and litter solutions, and concentrations generally decrease with soil depth (Table 1). Relatively little information exists about the relationships of such soluble organics to the cycling of inorganic elements, although the latter has been studied alone in great detail as exemplified by numerous other papers in this volume. Clearly, more attention must be given to the organic fraction if we are to better understand the mechanisms of the cycling and interactions of organic and inorganic components in forested ecosystems.

Table 1. Dissolved organic C (DOC) in solution moving through the canopy, litter, and soil of mixed-conifer forests at Blodgett and Challenge Forest sites in northern California, 1987. Soils are a Pachic Xerumbrept at Blodgett and an Ultic Haploxeralf at Challenge.

	DOC (mg L^{-1})†	
	Blodgett site	**Challenge site**
Throughfall:		
Canopy edge	2.0 ± 0.6 (10)	3.2± 3.2 (8)
Dense canopy	13.3 ± 6.9 (10)	7.3± 2.1 (8)
Stemflow	40.9 ± 61.0 (8)	32.6 ± 26.5 (11)
Litter Solution	45.9 ± 29.1 (16)	31.7 ± 15.0 (14)
Soil Solution:		
25 cm depth	8.9 ± 7.5 (8)	16.0 ± 5.6 (6)
100 cm depth	2.8 ± 1.4 (9)	6.8 ± 3.1 (7)

† x ± SD (n)

Leaching experiments. We first conducted a general study in which a wide array of forest and range soils in California were leached with inorganic acid. The results of this leaching study illustrate some of the main interactions between pH, soil organic matter and cation leaching.

Samples from the A-horizon of 23 soils having various parent materials were selected (McColl 1981); many of the samples were from the standard pedon that typifies the particular series. Properties of the 23 soils are given in Table 2. For these surface soils as a whole, the organic carbon fraction contributed more to the CEC than did the mineral fraction (Table 2), and the correlation between CEC and organic carbon was highly significant (r =

0.81, $p < 0.001$), whereas the correlation between CEC and the clay fraction was non-significant ($r = 0.14$, $p < 0.05$).

Table 2. Surface soils grouped according to the shape of their curves of Al leached by acid inputs; groups correspond to those of relatively high and low organic-C content

Soil Series	Particle Size S	Si	C	pH	Org.-C (pct.)	C.E.C ($mol_c\ kg^{-1}$)	Base sat. (pct.)	†Organic fraction contribution to C.E.C. (pct.)
A - Soils with organic-C of 4.8 ± 1.4 (pct.):								
Chaix	50	38	12	5.6	6.03	0.278	58	61
Chawanakee	77	22	1	5.6	4.04	0.161	60	77
Chiquito (1)	71	23	6	4.5	5.16	0.165	18	88
Chiquito (2)	73	22	5	4.6	5.37	0.185	25	82
Corbett	75	24	1	4.7	4.97	0.126	34	100
Josephine	33	43	24	5.7	4.35	0.206	77	59
McCarthy	69	23	8	5.2	6.64	0.241	42	77
Musick	54	36	10	5.7	5.55	0.220	76	71
Neuns	37	49	13	5.3	3.14	0.176	59	50
Shaver (1)	59	36	6	5.4	6.04	0.245	61	69
Shaver (2)	56	39	4	5.8	7.21	0.351	94	58
Sites	27	48	25	4.5	4.46	0.223	30	56
Windy	54	45	1	5.1	4.89	0.243	51	56
B - Soils with organic-C of 2.4 ± 1.1 (pct.):								
Aiken	33	41	26	5.3	3.65	0.201	57	51
Argonaut	29	51	20	5.5	2.06	0.121	79	46
Auberry	69	23	8	6.1	1.15	0.069	81	47
Cohasset	29	56	15	5.8	2.35	0.221	53	29
Dubakella	20	58	22	5.4	4.15	0.232	79	50
Hesse	32	47	21	5.9	1.09	0.117	68	50
Holland	55	34	11	5.8	2.74	0.140	71	55
Sheetiron	49	28	23	5.2	3.41	0.167	69	57
Vista	75	21	4	6.0	1.85	0.124	70	58
Yolo	65	20	15	6.8	1.32	0.187	75	20

†Calculated from the mean value of 1.63 mol (+) kg^{-1} O.M. (Helling *et al.* 1964).

Triplicate soil samples (5.0 g) were leached for two hours with H_2SO_4 + HNO_3 (50 mL) at pH 2.0 to 6.0, and properties of the leachates determined. Uniform leaching rate was maintained using a mechanical leaching device (Holmgren *et al.* 1977). Leachate Al was determined by the modified aluminon method (Jayman and Sivasubramanian 1974), other cations by atomic absorption spectrophotometry, and DOC using a carbon analyzer with infra-red detector.

Leaching curves for two of the 23 soils are shown as examples in Fig. 1. The Chiquito series is a Ruptic Lithic Cryumbrept at 2,835 m elevation in the mid-Sierra Nevada close to the timberline, and the Vista series is a Typic Xerochrept at 250 m elevation in the foothills supporting annual grasses and scattered oaks. Both soils are derived from similar granitic parent material. Curves for leaching of exchangeable ions (Ca^{2+}, Mg^{2+}, K^+) were relatively simple (McColl 1981) and were of a similar shape to the curves of H^+, as illustrated by the "acidity" curve in Fig. 1.

Curves for the leaching of organic carbon over the pH range also were similar. Much more soluble organic-C is leached from the Chiquito than the Vista, which reflects the higher organic-C content of the Chiquito (Table 2).

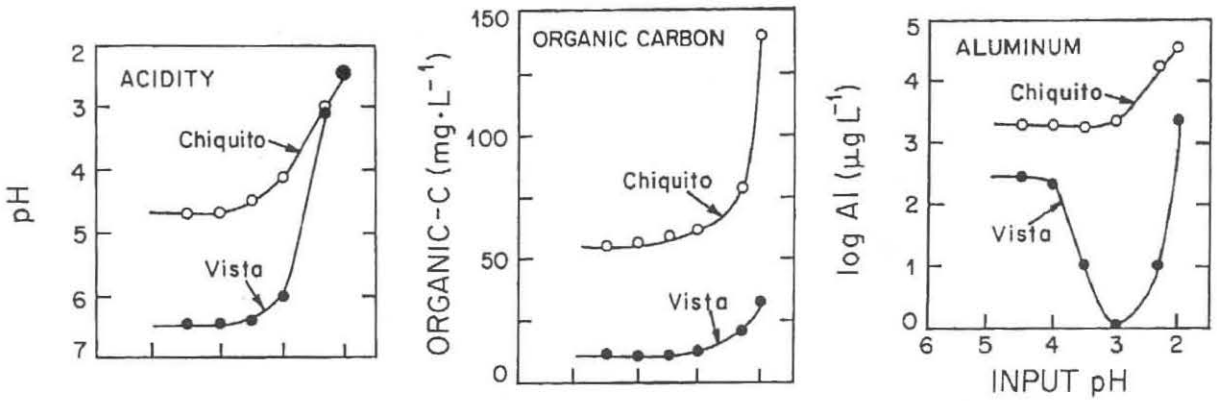

Figure 1--Effect of pH treatment on pH, organic-C and Al in leachate from A-horizon samples of Chiquito and Vista soil series; both are granitic, but have organic-C contents of 5.37 and 1.85%, respectively.

By contrast, mechanisms of leaching of metals such as Al, Fe and Mn are more complex. For some soils such as the Chiquito, leaching curves for Al (Fig. 1) are similar to those of the exchangeable cations. In other soils such as the Vista, there is a marked decrease in Al leached over the mid-range of H^+ input (Fig. 1). Soils showing the decrease in the mid-range of the leaching curve for Al had a mean (± SD) organic-C content of 2.4 ± 1.1 percent, whereas other soils had 4.8 ± 1.4 percent; the difference between the mean organic-C of the two groups of soils (distinguished in Table 2) is highly significant (Student's t-test; $p < 0.001$).

Implications regarding acidic atmospheric deposition. Soils with high organic carbon had greatest Al in leachate (e.g., Chiquito soil in Fig. 1), presumably due to the presence of organo-Al complexes. Only in the more-acid treatments (pH inputs < 2.7) did acidity *per se* become the overriding factor in Al leaching, most likely as Al^{3+}. In soils such as Vista with lower organic carbon content, amounts of Al leached were very low in the mid-pH-range treatments (Fig. 1). This pH range is broad due to various interactions between solid and solution phases, which differ between samples taken at different soil depths. Over the pH range of minimum-soluble Al, a precipitate of Al-hydroxide complex probably is formed. This type of phenomenon has also been noted by Prenzel (1982) studying leachates from acid forest soils in Germany that receive high sulfate inputs from acidic atmospheric deposition. He suggested the formation of a mineral such as jurbanite (Anthony and McLean 1976), but this mineral was not identified. The precipitate is likely to be complex in composition and could well be comprised of Al, Fe and other insoluble metal hydroxy-sulfates. The mineralogical composition of the soil and the chemical composition of the leaching solution would be the main factors determining the nature of the chemical complex (Garrels and Christ 1965).

These results suggest that organic matter, within the mineral soil profile and as litter, plays an important role in the solubilization and mobility of Al (and other metals such as Fe and Mn) in forest soils.

There are practical implications of these interactions. Soils low in organic matter are more susceptible to changes in leaching of these metals when impacted by acidic atmospheric deposition. However, these changes may not necessarily be exhibited as increased losses in leachate if acid inputs accompanied by SO_4^{2-} are not severe, because meta-stable insoluble metal precipitates may be formed. These complex metal hydroxides or sulfates could act as temporary storage components for toxic metals such as Al, and also of SO_4^{2-}, and it is possible that a cyclic pattern of retention and release of Al and SO_4^{2-} could occur under varying acidic inputs (Nordstrom 1982). On shallow, neutral-to-acid soils that are low in organic matter, accelerated leaching losses of soil Al and similar metals are likely to occur only under conditions of severe acidic atmospheric inputs.

In soils with high organic matter, leachate concentrations of soluble organics are likely to be high, and metal complex formation could result in leaching of Al. Mobility of such complexes depends on soil-profile characteristics, flow rates and other characteristics as the solution moves laterally or downward in the soil profile. However, soil organic matter in undisturbed forests is usually great enough to absorb small to moderate acid input without marked increase in Al leaching (Fig. 1).

SOLUBILIZATION OF SOIL ALUMINUM BY ORGANIC ACIDS

Metal-complexing Ability Of Litter Extracts

How effective are soluble organic acids leached from litter and soil in solubilizing metals from forest soil? To answer this question a typical mid-elevation Sierra Nevada soil developed on granodiorite parent material (Pachic Xerumbrept, Shaver series) was leached with extracts of O_1 litter from bracken fern (*Pteridium aquilinum* (L.) Kuhn) and incense-cedar (*Calocedrus decurrens* Torr.), and with citric and nitric acid, acidified at pH 2.8. Leached Al was determined. Methods are given by McColl *et al.* (1987).

The complexing ability of the litter extracts far exceeded the effectiveness of nitric acid and was about half as effective as citric acid in solubilizing Al from the soil (Fig. 2). Bracken fern extract contained 787 mg L^{-1} DOC, 53 percent of which was organic acid, and the incense-cedar contained 812 mg L^{-1} DOC, with 41-percent organic acid (McColl *et al.* 1987, Pohlman and McColl 1988). Therefore, effectiveness of leaching by the organic acid fraction

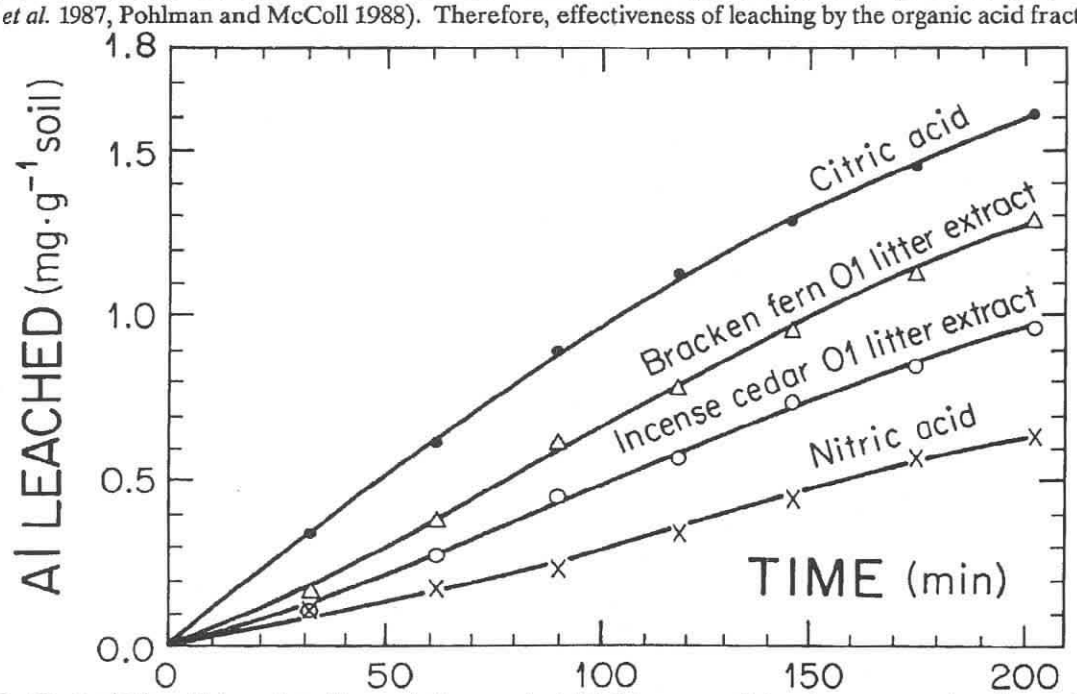

Figure 2--Cumulative Al leached by solutions at pH 2.8 from an A-horizon sample of granitic soil from Blodgett Forest, illustrating relative effectiveness of litter extracts (from McColl et al. 1987).

of these litter extracts approximated that of citric acid. On this basis we used citric acid as a model organic acid in Al-leaching studies described below.

Solubility Of Solid-phase Components Of Soil

The solubility of solid-phase Al within different size-fractions of the A-horizon of a soil at Blodgett Experimental Forest, northern California, was evaluated. Detailed methods and results are given by Jersak and McColl (1989). The granitic soil (Pachic Xerumbrept) was fractionated into particle-size classes, and the nature and sizes of the solid-phase Al pools were determined. The size-fractions also were leached with citric acid of the same concentration used earlier (Fig. 2), and the rates and cumulative amounts of Al release were compared with the solid-phase pools determined. Results for the coarse-silt fraction are given in Fig. 3 as an example. The Al released rapidly in the early stages of leaching quantitatively corresponded to the organically-bound Al (quantified by Na-pyrophosphate extraction), indicating that this was the most soluble Al pool in the solid phase of the soil. Subsequent leaching of Al, which was steady but slower, was from the solubilization of primary and secondary crystalline lattice minerals. It is reasonable to assume, therefore, that most soil Al leached by intermittent wetting-fronts under field conditions comes from the organically-bound soil Al fraction.

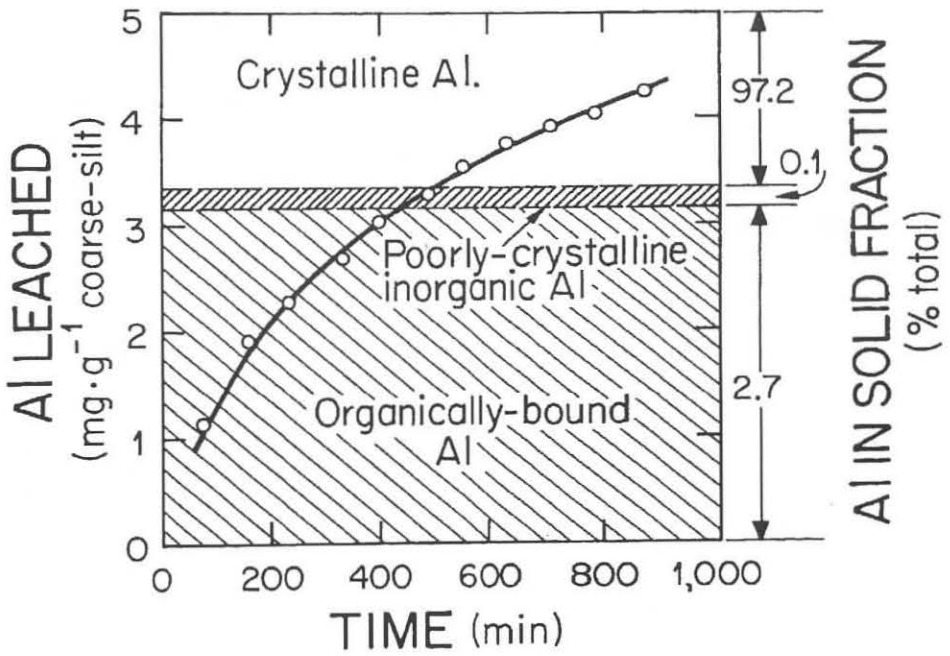

Figure 3--Graphical superimposition of cumulative Al leached by citric acid, over solid-phase Al pools in the coarse-silt fraction of the A-horizon of soil from Blodgett Forest (from Jersak and McColl, 1989).

FRACTIONATION OF SOLUBLE ORGANICS AND ALUMINUM

Organic Fractions And Their Relationships To Metal Leached

We examined the main components of dissolved organic carbon (DOC) of litter extracts and determined which are most closely correlated with metal leaching (Pohlman and McColl 1988). Soluble organics from litters collected

at two field sites in northern California (Blodgett and Challenge Experimental Forests) were fractionated into hydrophobic and hydrophilic acid, base, and neutral classes using methods outlined in Fig. 4. The methods used were based on the research of Junk *et al.* (1974), Leenheer and Huffman (1976) and Keefer *et al.* (1984).

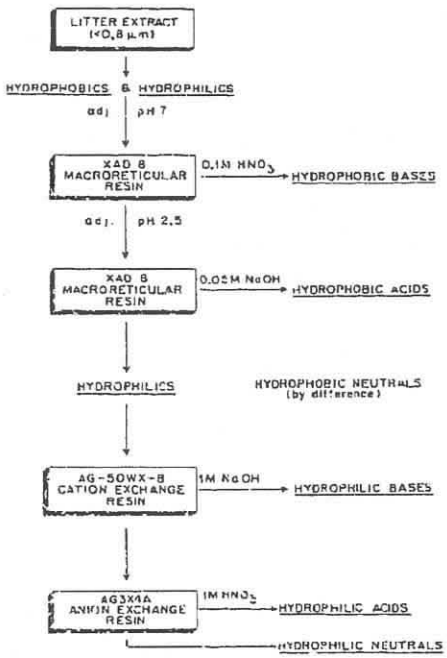

Figure 4--Flow chart for DOC fractionation of litter organics (from Pohlman and McColl 1988).

The major classes of compounds found in all leachates were acids and neutrals (Table 3). The quantities of classes were proportional to total organic C dissolved; hydrophobic plus hydrophilic acid-C, base-C, and neutral-C contents for all litters corresponded to the following: (mean ± standard deviation) 49.6 ± 5.6 percent, 8.8 ± 3.7 percent, and 41.1 ± 7.9 percent, respectively. The total acid content constituted 30.6 ± 5.9 percent hydrophobics and 18.9 ± 5.9 percent hydrophilics.

High correlations were found between dissolved Al and Fe and hydrophilic organics, hydrophobic acids and bases, and polyphenolics when litter over soil was leached (Table 4). The organic acids, especially polyphenols, are the most chemically active class of organics in the DOC group because they contain functional components that can chelate and dissolve Al and Fe from mineral matter. Soluble polyphenolics, which include tannins, constituted about 10 to 23 percent of the DOC content of both O_1 and O_2 litter extracts (Table 3). The contribution of bases to the overall dissolution process was less important because of their relative small content vis-a-vis other classes of organics found in leachates.

These results illustrate that there is a direct relationship between organics released from litter and Al and Fe dissolved from the underlying soil. In contrast, if litter alone is leached, i.e. without soil beneath, there is no significant correlation between DOC and metals in leachate (Pohlman and McColl 1988). Litter itself can also be a source of some of the metals that move in the soil solution. Plants that accumulate metals will obviously have the highest metal concentrations in litter.

In the following sections we examine the particular fraction (rather than just the total amount) of the metal components of soil that are complexed and leached with soluble organics in the soil solution. We also examine the particular organics compounds of soil and litter solutions, and identify those with greatest metal-complexing abilities, and we examine the effect of pH.

Table 3. Distribution of hydrophobic and hydrophilic acid, base, and neutral C and polyphenolic C content of litter leachates (from Pohlman and McColl 1988).

		Hydrophobic			Hydrophilic			
Litter type	DOC	Acid	Base	Neutral mM	Acid	Base	Neu-tral	PP[†]
				Blodgett site, sampled July 1985				
Incense-cedar O_1	68.2	16.6	2.0	12.4	11.6	1.6	21.4	9.0
Incense-cedar O_2	12.8	4.2	0.4	1.0	2.0	1.0	4.2	1.2
Ponderosa pine O_1	14.0	2.8	0.4	1.4	2.8	1.0	6.6	1.5
Ponderosa pine O_2	6.7	2.0	0.2	0.2	1.2	0.6	3.0	0.8
Tanoak O_1	50.0	18.6	1.8	12.2	4.4	1.4	9.2	9.4
Tanoak O_2	5.3	1.4	0.2	0.2	1.4	0.8	1.4	0.8
				Blodgett site, sampled June 1986				
Bracken fern O_1	16.5	5.4	0.6	0.4	3.4	1.0	5.4	2.1
Douglas-fir O_2	23.8	6.3	0.3	4.7	7.5	1.2	3.0	ND.[‡]
White fir O_1	42.7	14.4	1.2	6.4	6.6	1.0	11.0	6.2
				Blodgett site, sampled August 1985				
Bracken fern O_1	71.0	24.2	1.3	1.3	13.5	4.7	22.5	16.0
Ceanothus sp. O_1	59.0	17.8	1.7	10.7	11.2	1.8	16.0	10.6
Douglas-fir O_1	27.2	7.2	0.7	4.8	5.2	1.2	7.0	3.2
Douglas-fir O_2	5.0	2.2	0.2	0.2	0.8	0.8	1.2	1.1

[†]PP = polyphenolic C.

Table 4. Simple correlation coefficients between litter organics and soil dissolved metal content of leachates from underlying soil (from Pohlman and McColl 1988)

Organics	Al	Fe
Hydrophobics		
Acid-C	0.91***[†]	0.71**
Base-C	0.82***	0.54*
Neutral-C	0.57*	0.85***
Hydrophilics		
Acid-C	0.93***	0.85***
Base-C	0.90***	0.82***
Neutral-C	0.95***	0.79***
Polyphenolic-C	0.94***	0.80***

[†]*,**,*** *r* values significant at p = 0.05, 0.01, and 0.001 respectively; n = 13.

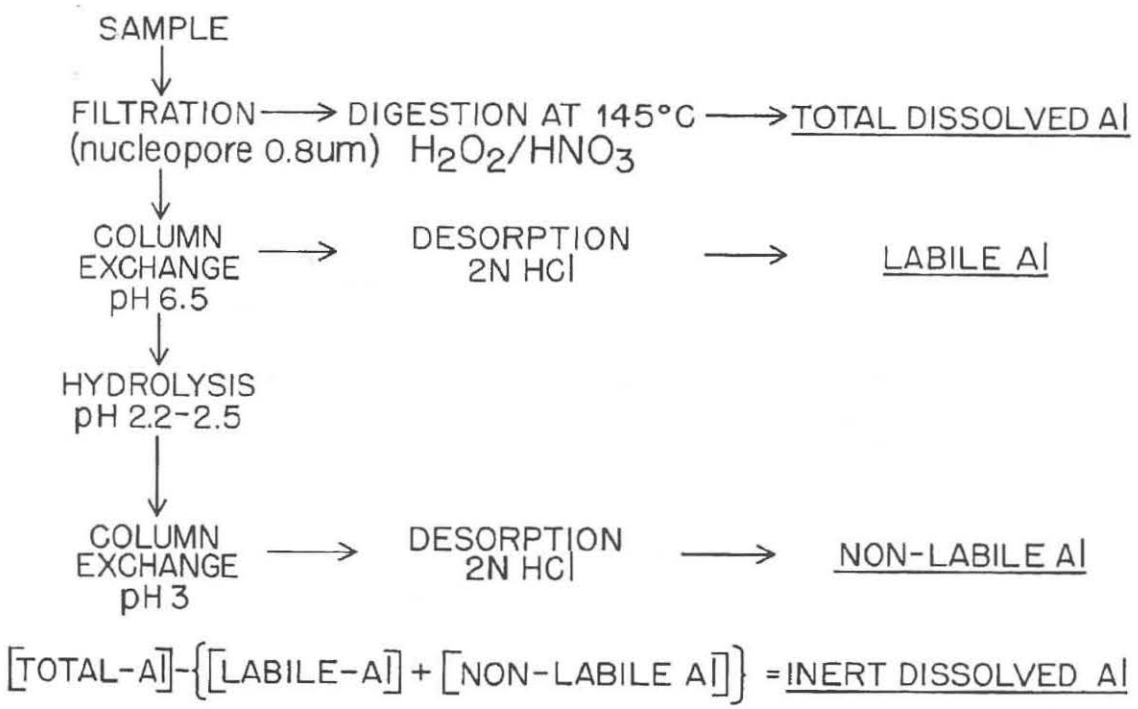

Figure 5--Flow chart for Al fractionation of soil and litter solutions.

Aluminum Fractions And pH Effect

Aluminum fractionation. There are many procedures for Al-fractionation (e.g. Driscoll 1984, James *et al.* 1983, May *et al.* 1979, Shotyk and Sposito 1988, Turner 1969). They include the techniques of exchange-resin, complexiметry, fluoride electrode and fluorescence quenching. Our exchange-resin method is based on the fact that different Al-complexes are stable in different pH regimes; the Al-fractions designated are similar to those of Driscoll (1984). Our Al-fractionation method is summarised in Fig. 5; further details are available on request.

Labile-Al includes monomeric inorganic species and organo-Al complexes that are easily dissociated by a Chelex resin exchange column at neutral pH. The non-labile species include organo-Al complexes that are kinetically stable at neutral pH, but can be dissociated by acid hydrolysis and resin exchange. The inert Al species include complexes that are kinetically stable at an acid pH. This fraction includes slowly-dissociated organo-Al complexes (e.g. fulvic-Al) and possibly slowly-exchangeable Al bound in colloidal matter.

Leaching experiments using soil and litter-over-soil. Aluminum fractions in a number of different types of litter and litter-over-soil extracts are presented in Table 5. The quantities of labile, non-labile, inert Al, and DOC found in litter leachates varied widely between the different litter types. There was little relationship between DOC and the different species of Al found in the solutions. This diversity in the quantities of Al and organics released by the different litter types is attributed to the inherent differences of chemical constituents of the litters at the time of sampling, rather than to differences between plant species. Plant species that are Al-accumulators would have high Al concentrations in litter. Future studies should address such plant differences.

In contrast, when leaching was conducted through litter-over-soil, the quantities of total Al leached increased significantly over the quantities of Al released from the respective litters, and from the respective soils in the absence of litter. Again, this indicates that organics released from litters contained components with high Al-complexing

Table 5. Estimation of Al species in litter and soil extracts.[†]

Litter/soil	pH	DOC	Labile Al	Non-labile Al	Inert Al	Total[‡] Al
		mmol L^{-1}		μmol L^{-1}		
Incense-cedar O_1/none	4.30	57.0	2.7	1.9	0.0	3.1
Incense-cedar O_1/Blodgett A	5.54	56.4	74.6	92.7	0.0	166.0
Incense-cedar O_2/none	5.67	11.4	0.0	1.9	4.6	6.5
Incense-cedar O_2/Blodgett A	5.53	9.2	14.3	14.1	10.4	38.8
Ponderosa pine O_1/none	4.40	10.8	6.2	10.8	0.7	17.7
Ponderosa pine O_1/Blodgett A		5.65	11.4	11.4	17.3	2.8
Ponderosa pine O_2/none	4.50	6.7	7.5	10.6	0.0	16.9
Ponderosa pine O_2/Blodgett A		5.39	6.8	8.3	9.1	16.8
Tanoak O_1/none		4.60	41.8	3.1	10.8	0.7
Tanoak O_1/Blodgett A		5.46	42.5	32.9	52.7	2.2
Bracken fern O_1/none		5.27	47.9	0.0	0.0	1.5
Bracken fern O_1/Challenge A	5.21	59.4	90.9	107.5	55.6	254.0
Ceanothus sp./none		5.30	47.3	12.1	6.2	2.3
Ceanothus sp./Challenge A	5.29	44.5	70.4	128.0	1.6	200.0
Douglas-fir/none		5.08	28.5	19.9	10.0	3.6
Douglas-fir/Challenge A		5.21	26.5	38.0	19.2	17.8
None/Blodgett A		5.43	0.5	1.0	2.5	12.1
None/Challenge A		4.90	0.9	1.8	2.8	8.8

[†]Extracts were prepared by leaching 5.0 g (< 200 μm) soil, 1.0 g (<500 μm) litter, or litter-over-soil with pH 3, HNO_3 solution. Extracts were filtered through 0.8 μm nucleopore filter and speciated immediately. Extractions were conducted at 0.70 mL min^{-1} with 50.0 mL volume input. The values represent mean values of three replicate extractions.
[‡]Total Al was determined independently according to scheme in Fig. 5.

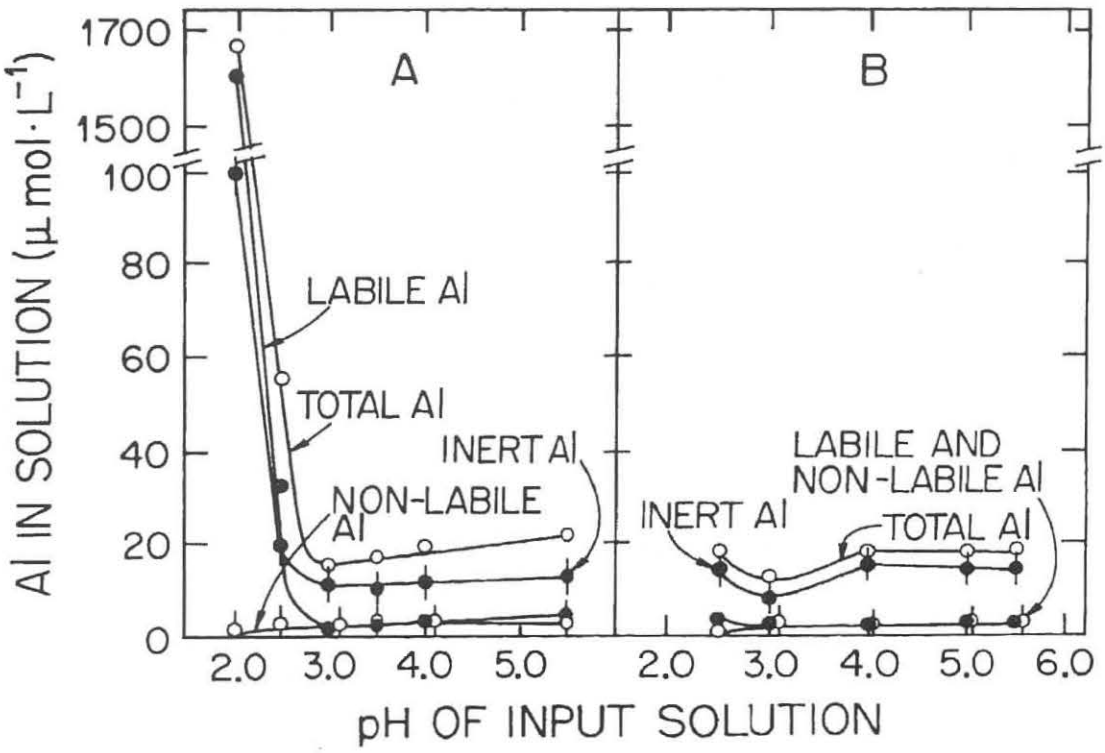

Figure 6--Effect on pH of input solution on leaching of different species of Al from (A) Blodgett Forest, and (B) Challenge Forest soils.

abilities, and dissolution of Al from soil components was by chelation with these organic constituents. In addition, labile, non-labile and total Al was highly correlated ($p < 0.001$) to DOC released from litters ($r = 0.94$, 0.88 and 0.90, respectively). For most litter-over-soil leachates the quantities of non-labile Al exceeded the quantities of labile Al by 1.1 to 1.8 times. The reverse situation was found for the Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) litter/Challenge A horizon combination where quantities of labile Al were about twice the quantities of the kinetically more stable non-labile Al species. The lability of the Al species was due to either the rapid dissociation of complexed Al into monomeric species, and/or to the degree of complexation with organic constituents during the dissolution process. The latter process would be a function of the type and concentration of active chelating agents dissolving from the litter layer.

Inert Al species were not significantly correlated with DOC content of leachates. Inert Al was the major species found in soil leachates from both sites. The flux of soluble organics through the soils tended to modify the content of inert Al in the extract.

The effect of input pH on Al fractions in soil extract is presented in Fig. 6. With increasing acidity in the input solution the quantities of labile, non-labile and inert Al in Blodgett soil leachate remained fairly constant from pH 5.5 to pH 3.0 (Fig. 6A). The main Al species over this range of H^+ input was inert Al, and the concentrations of labile Al and non-labile Al were about equal. Similar results were obtained with Challenge soil leachates (Fig. 6B) except that there was a slight decrease in inert Al between pH 4 and pH 2.5. Leaching of Al over this pH range represents "background" leaching where dissolved Al is probably generated from *in situ* soil organic matter by mass flow action of percolating solutions, as was also observed in earlier leaching experiments (Fig. 1).

When acidity in the input solution of Blodgett soil was increased to 10^{-2} M H^+, about 2-fold more DOC was dissolved, and substantially more labile Al and inert Al were dissolved over and above the "background" leaching levels; at pH 2 input solution, dissolved Al in the extracts was composed of 94 percent labile Al and 6 percent inert Al. This shift to labile Al as the dominant form, along with increased acidity (pH 3.2) of extracts, suggests that H^+ dissolution of inorganic constituents had occurred, releasing monomeric Al species. About 8-fold more inert Al was released over and above the "background" level by the higher acid input.

Relative toxicity of Al fractions. Although we have not studied the bioavailability and toxicity of soil Al, it is worth noting that these characteristics differ within the main Al fractions (or "Al species", as they are often termed), and that there are practical implications of these differences. Organic complexes of Al have been found to be non-toxic to plants, whereas inorganic Al species are phytotoxic (e.g. Adams and Moore 1983, Hue *et al.* 1986).

The experimental results and conclusions of Hargrove and Thomas (1981) illustrate the practical importance of these differences in phytotoxicity of Al species: They found that increasing soil organic matter resulted in lower exchangeable Al at any given pH, and decreased the soil pH at which Al toxicity occurred. Thus plants grew better at any given pH with increasing organic matter levels. Their results help explain why plants are often able to grow better at lower pH in organic soils than at low pH in mineral soils. These results lead to the conclusion that organic matter, such as farm manure or sewage sludge, added to acid soils or drastically disturbed lands that are very acid, would help reduce Al toxicity by complexation of Al with the organic matter.

ORGANIC COMPLEXATION OF SOIL ALUMINUM

Effective Organic Acids

To further elucidate mechanisms of metal complexation, free organic acids in the hydrophobic and hydrophilic acid groups of litter leachates were identified using HPLC techniques (McColl and Pohlman 1986, Pohlman and McColl 1986, 1988). The HPLC chromatograms for Douglas-fir and ponderosa pine (*Pinus ponderosa* Laws) litter extracts are shown in Fig. 7 as examples. High correlations were obtained between free-organic acid-C content of litter extracts and Al ($r = 0.87$, $p < 0.001$) and Fe ($r = 0.82$, $p < 0.001$) dissolved from soils.

Several of the free-organic acids identified exhibit high metal complexing properties. Through chelation, oxalate and malate are very effective in preventing the precipitation of phosphate by Al and Fe (Struthers and Sieling 1950). We found that malic acid was 3 to 5 times faster in dissolving Al from two forest soils than other dicarboxylic acids

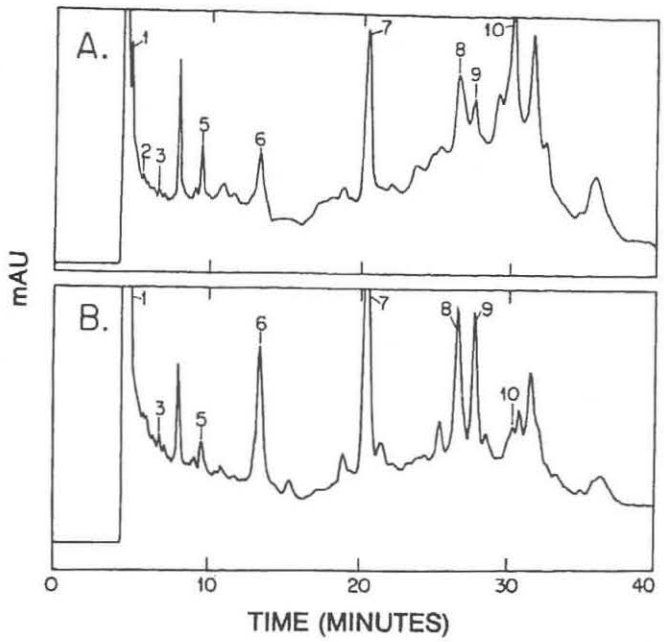

Figure 7--HPLC chromatograms at 210 nm UV wavelength showing free organic acids from (A) Douglas-fir O_1, extract concentrated 40-fold, and (B) ponderosa pine O_1, extract concentrated 62.5-fold. Numbers refer to identified acids as follows: 1 Oxalic, 2 Maleic, 3 Aconitic, 4 Fumaric, 5 Gallic, 6 Protocatechuic, 7 "p"-Hydroxybenzoic, 8 Vanillic, 9 Benzoic, 10 p-Coumaric (from Pohlman and McColl 1988).

such as aspartic and maleic acids. We also found that gallic acid was 3 to 5 times more effective as a chelator of Al than "*p*"-hydroxybenzoic acid, and found protocatechuic acid to dissolve Al about 4 times faster than *p*-hydroxybenzoic acid (Pohlman and McColl 1986). Free-organic acids such as oxalic, malic, gallic, and protocatechuic could be classified as having high complexing abilities, and they made up 60 to 80 percent of the identified free-organic content of litter extracts (Pohlman and McColl 1988). We conclude that organic compounds such as di- and tri-carboxylic acids containing β-hydroxy functional groups, and phenolic acids containing ortho-OH groups are more effective chelators of Al than other similar compounds with other functional group combinations. This is because these organic acids apparently are able to form stable 5- and 6-membered ring structures with metals (McColl and Pohlman 1986, Pohlman and McColl 1986).

Effect Of pH And Competing Cations

Environmental perturbations such as that from acidic atmospheric deposition, which may change the soil pH, could result in increased leaching of soil Al. Thus, the question arises: besides releasing Al from minerals, how will H^+ compete with Al for the anionic sites and affect the binding of Al to organic ligands? Furthermore, what will be the effect of increased acidity on competition between Al and other cations such as Ca? To answer these questions we examined Al- and Ca-binding at pH 4.5 (the acidity documented in some areas most affected by "acid rain") (Tam and McCol l 1990) and at pH 5.7 (the acidity of water in equilibrium with atmospheric CO_2) .

We used a comparative approach by examining the relative binding affinities of various organic ligands to Al, and also to Ca. We chose Ca as a contrast because it is a biologically essential element responsible for a vast number of metabolic functions. Based on the ionic potential and the consequent chemistry, Ca and Al are competitive. The technique we used (Tam and McColl 1990) was modified from mobile-phase ion-pairing chromatography

(MPIPC), in which a solution containing the metal (Al or Ca) which binds to the organic ligand, is used to elute the latter from an anion-exchange column. The basic scheme may be represented as:

$$(R^{+}\text{-- }OR'^{-})_{(s)} + M^{+}_{(m)} + A^{-}_{(m)}\ (R^{+}\text{--}A^{-})_{(s)} + (M\text{--}OR')_{(m)}$$

where, (s) is the stationary phase and (m) is the mobile phase. For simplicity, the components are represented as single-charged species only.

We found that at pH 5.7, the Al-binding affinity of the following group combinations was found to decrease in the order:

$$\underline{COOH\ \ OH} > \underline{COOH\ \ COOH} > \underline{COOH} > \underline{OH\ \ OH}$$

whereas at pH 4.5, the order was:

$$\underline{COOH\ \ OH} > \underline{OH\ \ OH} > \underline{COOH\ \ COOH} > \underline{COOH}$$

The Ca-binding affinity, on the other hand, remained relatively unchanged at both pH's and decreased in the order:

$$\underline{COOH\ \ COOH} > \underline{COOH\ \ OH} > \underline{COOH} > \underline{OH\ \ OH}$$

In other words, Al is associated with phenolic (catecholic) and with carboxylic (phthalic) groups in more acidic situations (pH 4.5) whereas in less acid situations (pH 5.7), carboxylic groups have higher affinity. In contrast, Ca

Table 6. Effect of aging Douglas-fir O_l litter extract on disappearance of free organic acids

Acids and pH of leachate	Concentration after: 1 h	24 h	48 h
		(mM)	
1 Oxalic	TI†	TI	TI
2 Citric	TI	TI	TI
3 Aconitic	TI	TI	TI
4 Shikimic	4.2	4.2	3.0
5 Fumaric	3.6	1.9	TI
6 Gallic	0.3	0.0‡	0.0
7 Protocatechuic	7.2	4.2	TI
8 Gensitic	5.9	0.0	0.0
9 p-hydroxybenzoic	TI	TI	TI
10 Vanillic	5.7	3.5	2.5
11 Syringic	4.3	2.0	2.0
12 Benzoic	1.1	1.0	0.9
13 Ferulic	5.8	0.0	0.0
Total acids	38.1	16.8	8.4
Leachate pH	5.5	5.4	6.5

†TI - tentatively identified. Similar retention time (Rt) to standards, but UV spectra different.
‡Absence of peak at specific Rt or below concentration levels tested.

prefers carboxylic groups at both acidities. These results illustrate the complex consequences of increased soil acidity on metal leaching processes.

DISAPPEARANCE OF ORGANIC ACIDS IN FIELD LEACHATES

Analysis of Field Samples

One perplexing characteristic of soluble organic acids in leachates is that they are short-lived (Table 6) and cannot be found easily in soil and litter leachates in the field, thus making field sampling of solutions with lysimetry techniques difficult. This leads to the assumption by some researchers that the acids do exist, or that the products of their decomposition or polymerization are ineffective as metal complexing agents. In the following discussion we show that these two assumptions are incorrect.

We found that most simple organic acids were not identifiable even in fresh leachate sampled in the field using boro-silicate tension lysimeters, and analyzed in the laboratory a few hours later (Fig. 8). This suggests that decomposition and/or polymerization takes place rapidly. However, we experimented with a number of techniques and chemical extracts and found that organics that were extracted from litter leachates with ethyl acetate in the field immediately upon sampling were preserved, to the extent that reasonable differentiation of chromatogram peaks allowed detection and identification of specific organic acids (Fig. 9).

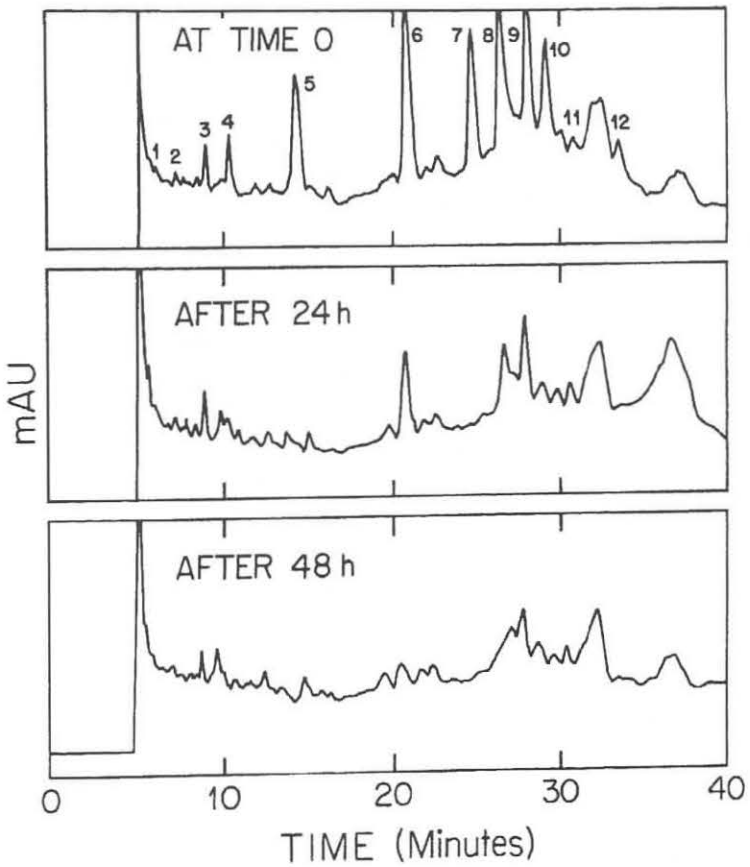

Figure 8--HPLC chromatograms at 210 UV wavelength showing disappearance of free organic acids from O_1, Douglas-fir litter extract, immediately analyzed, at 24 h, and at 48 h after sampling. Numbers refer to identified acids as follows: 1 Citric, 2 Aconitic, 3 Shikimic, 4 Fumaric, 5 Gallic, 6 Protocatechuic, 7 Gensitic, 8 "p"-Hydroxybenzoic, 9 Vanillic, 10 Syringic, 11 Benzoic, 12 Ferulic.

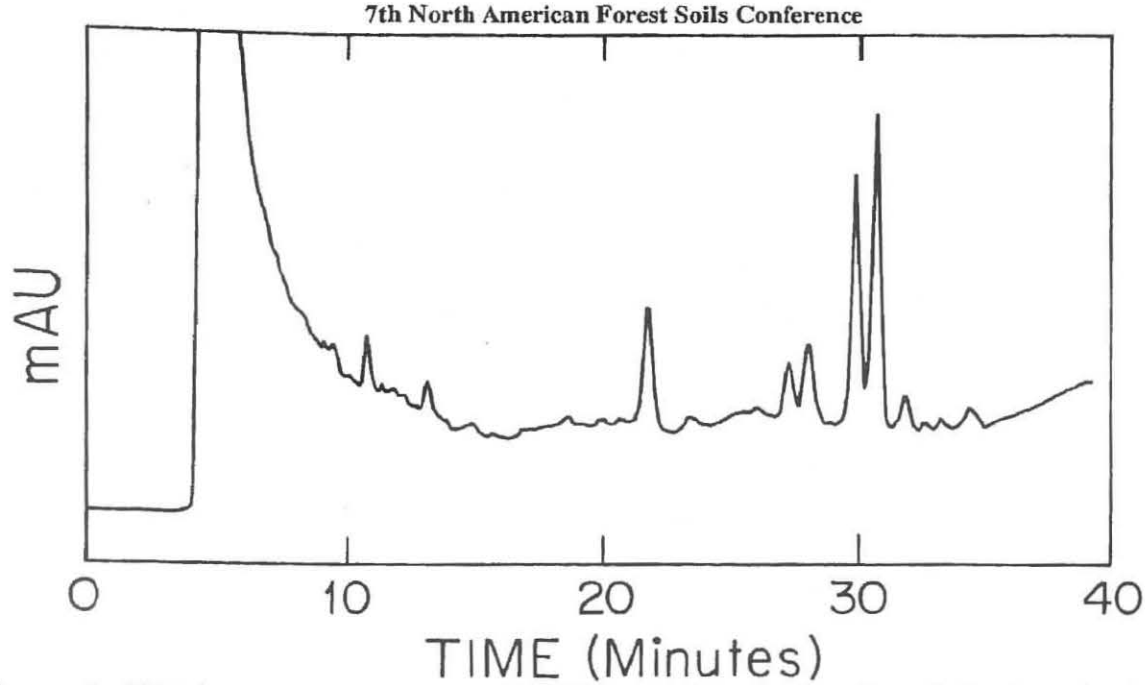

Figure 9--HPLC chromatograms at 210 UV wavelength showing distinct peaks for free organic acids from ponderosa pine litter that was immediately extracted with ethyl acetate after sampling at the Challenge Forest field site, then analyzed days later at the laboratory.

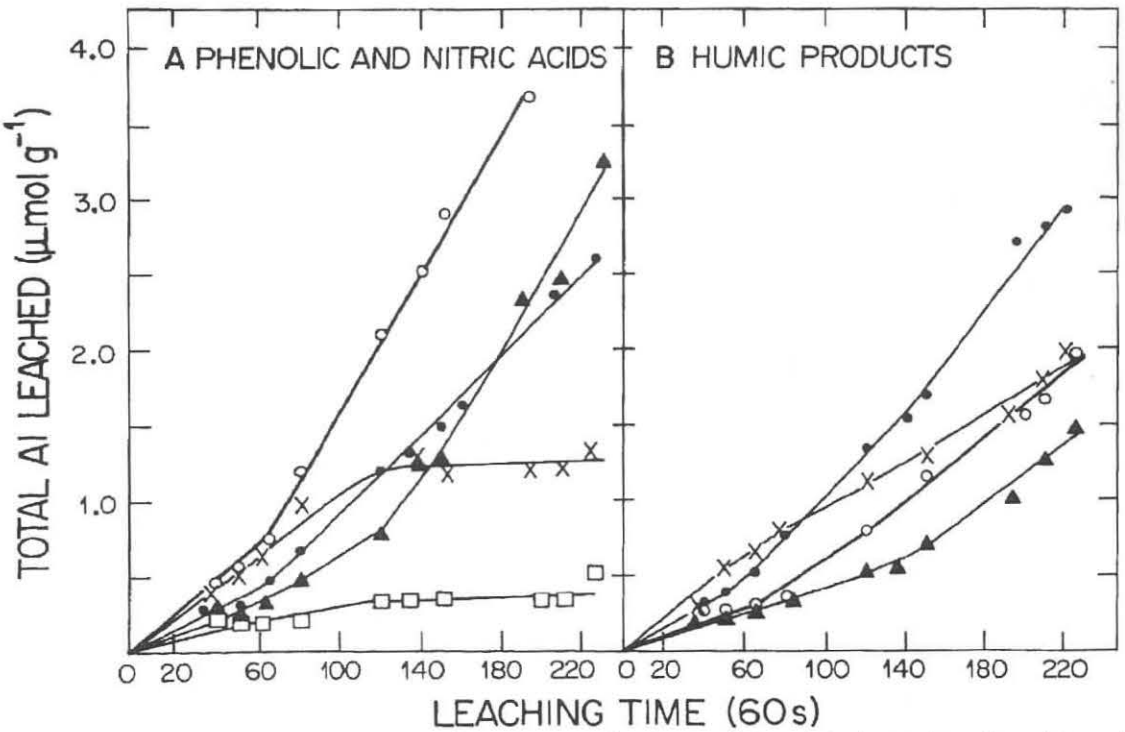

Figure 10--Rates of Al dissolution from Blodgett Forest A horizon soil in polyhydroxyphenolic acids and nitric acid are compared to dissolution in humic products of phenolic acids. (A) Dissolution in (●) 84.0 mg L^{-1} DOC gallic (pH 3.77), (X) 117.6 mg L^{-1} DOC syringic (pH 3.62), (O) 44.5 mg L^{-1} DOC 2,3-diOH (pH 3.14), and (▲) 91.0 mg L^{-1} DOC 2,5-diOH benzoic (pH 3.14) acids, and (□) HNO_3 (pH 3.68). (B) Dissolution in oxidation products of (●) 67.4 mg L^{-1} DOC gallic (pH 3.5), (X) 108 mg L^{-1} DOC syringic (pH 3.55),(O) 38.7 mg L^{-1} DOC 2,3-diOH (pH 3.13) and (Δ) 52.2 mg L^{-1} DOC 2,5-diOH benzoic (pH 3.15) acids. Initial pH of leaching solutions are in parentheses (from Pohlman and McColl 1989).

Formation Of Polymeric Humic Substances

The formation of polymeric humic substances from simple polyhydroxyphenolics is a complex process which can proceed both biologically (Sjoblad and Bollog 1981) and abiologically (Shindo and Huang 1984). The abiotic polymerization process has been attributed to manganese oxide surfaces (Stone and Morgan 1984). Oxidation of certain organics by Mn-bearing surfaces involves the reduction of Mn(IV) and Mn(III) to Mn(II) by organic reductants, and the process is accompanied by subsequent dissolution of Mn. Metal dissolution from solid soil constituents can thus be achieved by complexing and by oxidative processes.

The rapid disappearance of certain polyhydroxyphenolic acids in the presence of soil suspensions was accompanied by the dissolution of soil Mn and the formation of humic products (Pohlman and McColl 1989). Dissolution of Mn^{2+} from soil suspensions was attributed mainly to an oxidative process rather than a complexing process by the organic reductants.

We noted that humic products formed by the oxidative process were quite effective complexing agents (Pohlman and McColl 1989). The rates of Al dissolution from the Blodgett field site A horizon soil in humic products was comparable to the rates in the organic precursors, and were 3 to 6 times faster in dissolving Al than in mineral acid at comparable pH levels (Fig. 10).

CONCLUSIONS

1. Soluble organics in forest soil solutions come primarily from litter leachates, and secondarily from solubilization of organic matter in the mineral soil profile.

2. Organic acids including polyphenolics that are able to form 5- or 6-membered ring-structures with Al are the most effective organo-metal complexing agents. These include oxalic, malic, gallic and protocatechuic acids which make up 60 to 80 percent of the identified free-organic content of forest litter extracts.

3. The Al that is solubilized in surface soils high in organic matter largely comes from the organically-bound Al component of the solid-phase of the soil. Dominance of solubilized crystalline Al occurs only at low pH (~pH 3), in soils with low organic matter.

4. Acidity affects formation of different organo-metal complexes. In acid situations (pH 4.5), Al is primarily associated with phenolic groups, whereas in less acid situations (pH 5.7), carboxylic groups have higher affinity with Al.

5. Soluble organic acids in leachates in the field are short-lived due to decomposition and biotic and abiotic polymerization. Special techniques are required to sample and preserve soluble organics from field lysimeter installations.

6. Rapid rates of Al dissolution by short-lived products of organic acid polymerization relative to mineral acid indicates that abiotic oxidations are important in metal dissolution processes, in addition to metal complexation with soluble organics.

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